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Infrared absorption in bulk amorphous As

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We report the room-temperature infrared absorption spectrum of bulk a-As. The spectrum shows strong features in two well-separated spectral regions, near 230 cm and between 150 and 110 cm^{-1} The absorption in a-As is compared with absorption reported previously for a-Se and a-Ge. The absorption in all three elemental amorphous materials corresponds to structure in the vibrational density of states and is discussed in terms of a structural model that is based on the atomic coordination and resultant short-range order.

I. INTRODUCTION

We have measured the far infrared (ir) transmittance and reflectance of bulk samples of a-As, and have calculated the frequency dependence of the absorption constant. The occurrence of first-order ir absorption in an elemental solid is in itself an interesting subject. In crystalline solids, selection rules for ir activity are related to the symmetry and the atomic basis B, and can be determined from group-theoretical considerations. For an elemental crystal Zallen[1] has shown that first-order ir absorption is possible if there are at least three atoms in the unit cell. For those materials in which $B \geq 3$, only a small number of zone-center optic modes contribute to the first-order ir spectrum. Since the group-IV (C, Si, and Ge) and group-V (As, Sb, and Bi) crystals have a diatomic basis, $B = 2$, first-order ir processes are strictly forbidden. On the other hand $B \geqslant 3$ for the group-VI crystals and first-order ir has been reported in orthorhombic S,[2] α-monoclinic and trigonal Se,[3-5] and trigonal Te.[3,5,6] In an elemental amorphous solid, the absence of any long-range order relaxes selection rules so that in principle all of the vibrational modes can contribute to the ir absorption. First-order ir has been reported in a-Si,[7] a-Ge,[7,8-10] and a-Se.[3,4,11-13] In this paper we report the first measurements of ir absorption in a-As, and relate the features we find in that spectrum to gross structures in a vibrational density of states. Böttger[14] has noted that a wide variety of different experimental methods, including ir, Raman, electron tunneling, and inelastic neutron scattering, all give strong evidence that the density of vibrational states in a noncrystalline solid is governed primarily by the short-range order. In this paper we develop a simplified model for the vibrational density of states in an elemental amorphous solid and apply the model to a-Ge, a-Se, and a-As. The model is based on a local cluster that incorporates the essential elements of short-range order as they are determined by the chemical bonding.

The broad-band absorption of a-Si and a-Ge has been compared with a vibrational density of states derived from two different models. One model consists of a broadened crystalline density of states[7,15]; the second consists of a density of states derived from the application of a force-constant model to a continuous random network of tetrahedrally coordinated atoms.[16] These comparisons demonstrate that the ir and Raman spectra retain the gross features in the density of states, i.e., the number of peaks, their frequencies, and widths. Differences in the ir and Raman spectra are then attributed to matrix-element effects which vary slowly with frequency. In contrast, the much sharper ir absorption in a-Se has been interpreted in terms of the molecular species[17] which describe the short-range order of the amorphous solid.[4,11,12] Since the dispersion in the optic modes of a molecular system is inherently small, the molecular model is also in effect a density-of-states description. Brodsky and co-workers[18] have discussed the Raman spectrum in a-Te in terms of a density-of-states model, pointing out the universality in this type of interpretation.

The first-order ir absorption spectrum we report here for bulk a-As is in some respects intermediate to the spectra of a-Se and a-Ge. For example, the spectrum has strong features in two distinct spectral regimes as in a-Se; however the width of the dominant feature is about twice that in a-Se. The integrated absorption, or contribution of the optic modes to the dielectric constant, is larger than in a-Se, but smaller than in a-Ge. The gross features of the spectrum, in particular the occurrence of structure in two separated frequency regimes, are related in this paper to a density-of-states model that is based on the short-range order as determined by the coordination. This element of local order is also the basis for a random-network structure proposed by Greaves and Davis.[19]

II. EXPERIMENTAL PROCEDURES, RESULTS, AND DATA REDUCTION

The bulk samples of *a*-As used in this study were prepared by the pyrolysis of AsH_3.[20] This preparative technique yields large ingots with cm dimensions. Samples for the optical measurements were obtained by conventional cutting and polishing techniques. Reflectance measurements were made on a thick sample on which only one face was polished. Transmittance measurements were made on four samples of different thickness: 0.009, 0.018, 0.027, and 0.052 cm. ir spectra were obtained at room temperature using a Perkin-Elmer model 180 spectrophotometer operated in a double-beam mode. Resolution was approximately 2 cm^{-1}; reflectance and transmittance were accurate to ±0.01.

We found that the reflectance R was essentially independent of frequency in the regime from 100 to 1000 cm^{-1}, and equal to 0.29 ± 0.01. This corresponds to an optical-frequency dielectric constant ϵ_∞ of 11.1 ± 0.6. From the spacing of the interference fringes in the transparent region of the transmittance T of the 0.009-cm-thick sample, we calculate an index of refraction $n = 3.35$; this corresponds to $\epsilon_\infty = 11.2$ and is in excellent agreement with the value determined from the reflectance. The frequency dependence of the absorption constant $\alpha(\nu)$ is calculated using the usual relationship that is valid in those frequency regimes in which fringes are not resolved, i.e.,

$$T = \frac{(1-R)^2 e^{-\alpha d}}{1 - R^2 e^{-2\alpha d}} , \qquad (1)$$

where d is the sample thickness. Figure 1 gives the absorption spectrum as it is constructed from the transmittance data on the four samples; overlap between the $\alpha(\nu)$ calculated from the different samples was excellent and we estimate an uncertainty in $\alpha(\nu)$ of about ±5%.

The absorption spectrum is rich in structure between 100 and 500 cm^{-1}. The features that characterize the spectrum are (i) a relatively weak band at ~470 cm^{-1}, (ii) a slowly rising absorption from 400 to 300 cm^{-1}, (iii) a sharp, but weak feature at ~280 cm^{-1}, (iv) the dominant band centered at ~230 cm^{-1}, (v) a second sharp weak band at ~165 cm^{-1}, (vi) a relatively sharp band at ~145 cm^{-1}, and (vii) a broader feature at ~115 cm^{-1}.

Figure 2 is a comparison of the ir absorption spectra of *a*-Se, *a*-As, and *a*-Ge. The absorption at frequencies greater than 300 cm^{-1} can be shown to be due to higher-order processes through its temperature dependence. The point we wish to emphasize here is that whereas the spectrum of *a*-Ge is broad band with *three* distinct features, the spectra of *a*-Se and *a*-As show sharper features with the dominant absorption occurring in *two* distinct frequency regimes.

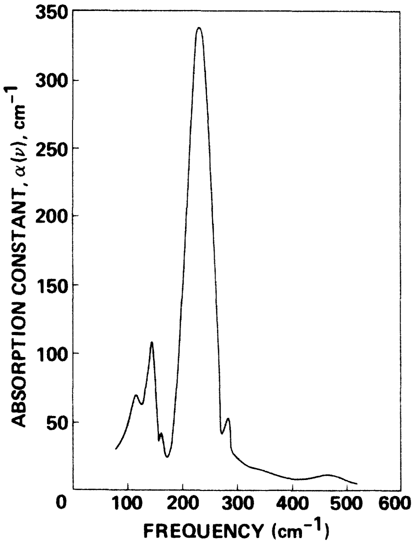

FIG. 1. Frequency dependence of the absorption constant of bulk *a*-As.

Another important aspect of the ir spectrum is the contribution of the ir modes to the dielectric constant. For *a*-Ge, Brodsky and Lurio[7] estimate a value of 0.3. For *a*-As we have calculated a value of ~0.1, whereas for *a*-Se we estimate a contribution of ~0.03. Thus in these three materials the contribution is largest in *a*-Ge and decreases in going to *a*-As and *a*-Se. These contributions to the dielectric constant correspond to average ir effective charges of ~$0.4e$ in *a*-Ge, ~$0.25e$ in *a*-As, and ~$0.15e$ in *a*-Se. This effective charge is a dynamic rather than a static property[21] and arises from a relaxation of selection rules rather than from a change in ionicity related to the chemical bonding in the amorphous phase.

III. DISCUSSION

Expressions have been presented that relate the ir absorption[9,10,21] or the Raman scattering[22,23] to a vibrational density of states. For example, Stimets *et al.*[9] have considered a medium in which the ir absorption arises from oscillators having a distribution of frequencies, and have found that

$$\nu\epsilon_2(\nu) = \frac{\pi}{2} \frac{4\pi N e^2}{M} f(\nu) g(\nu) , \qquad (2)$$

where ϵ_2 is the imaginary part of the dielectric constant, N is the density of oscillators, M is the oscillator mass, $f(\nu)$ is the oscillator strength, and $g(\nu)$ is a normalized density of states. $f(\nu)$ is also proportional to the square of the matrix element.[10]

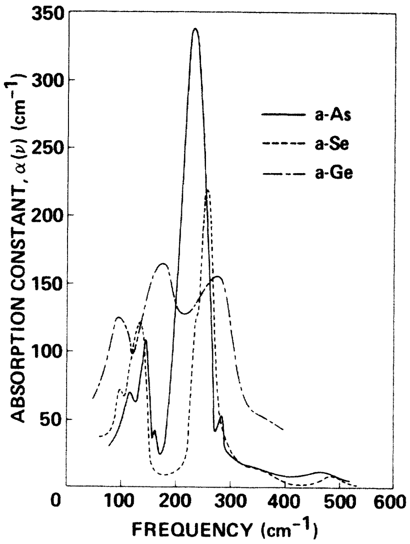

FIG. 2. Comparison of the absorption spectra of a-As with a-Ge and a-Ge. The spectrum for a-Ge is taken from the data of Ref. 9; the spectrum for a-Se is from the unpublished data of one of the authors of this paper (G. L.).

The absorption constant is simply proportional to $\nu\epsilon_2(\nu)$ through the index of refraction n; i.e.,

$$\alpha(\nu) = (2\pi/n)\,\nu\epsilon_2(\nu) \; . \tag{3}$$

In nondispersive media (n = const), such as the elemental amorphous semiconductors, $\alpha(\nu)$ is a direct replication of the vibrational density of states if $f(\nu)$ is frequency independent. In a similar way, expressions can be derived which relate the reduced Raman scattering to a product of a matrix-element term and a vibrational density of states.[10,22,23] Comparisons of the ir absorption in a-Si and a-Ge with model density of states[7,15] indicate that frequency-dependent matrix-element effects are important, so that the ir absorption is not simply related to a vibrational states through a single frequency-independent oscillator strength. On the other hand, the extension of these comparisons to the Raman scattering[15,16] demonstrates that the gross features in the vibrational density of states are preserved with different weighting factors in both the ir and Raman spectra.

Several approaches have been applied to the construction of model density-of-state functions for a-Si and a-Ge. These are based on a local coordination that is consistent with simple covalent bonding; e.g., in a-Ge and a-Si, the element of short-range order is a tetrahedral grouping of atoms. Smith *et al.*[15] developed a density of vibrational states by convoluting the crystalline density of states with a Gaussian function to remove the effects of long-range order. Alben and co-workers[16] constructed a density of states using a random covalent network and a simple force-constant model for the vibrational modes. Thorpe[24] developed a density of states by considering a small atomic cluster and determining boundary conditions on the surface atoms through the application of a self-consistent potential. The approach we take is similar to that of Thorpe,[24] but is more phenomenological in its form.

The vibrational density of states includes contributions from both acoustic- and optic-type modes. Taylor *et al.*[25] have studied the very-low-frequency or acoustic part of the ir absorption spectrum (~ 0.1 to 100 cm^{-1}) for a large number of amorphous materials including a-Se, a-Ge, a-As_2S_3, and a-SiO_2. They find $n\alpha(\nu) \propto \nu^{\beta}$ ($\beta \sim 2$) and conclude that the absorption is simply proportional to a structureless density of states. Our emphasis is on the absorption at higher frequencies, $\gtrsim 100\ \text{cm}^{-1}$ in a-Se, a-As, and a-Ge. This absorption is attributed to optic modes for which there is considerable structure in the density of states.

The optic-mode frequencies are determined primarily by short-range interatomic forces, associated for the most part with nearest- and next-nearest-neighbor interactions. Our model is based on the application of a force-constant model to the local clusters shown in Fig. 3. The information necessary to characterize these clusters is obtained from x-ray studies, primarily the radial distribution functions (RDF).[26–28] The information of importance is the bond length r_0, the bond angle θ_0, and the spread in these two parameters, Δr_0 and $\Delta\theta_0$, respectively. This information, along with a confirmation of the coordination, is contained in the first two peaks of the RDF.

The density of states we construct is based on the application of a two-parameter valence-force-field (VFF)[29] force-constant model to the clusters shown in Fig. 3. The force constants we employ are a bond-stretching force constant k_r, and a bond-bending force constant k_θ. Within this approximation, the energy per atom associated with changes in the bond-length, Δr, and the bond-angle, $\Delta\theta$, is given by

$$\Delta V = \tfrac{1}{2} k_r (\Delta r)^2 + \tfrac{1}{2} k_\theta r_0^2 (\Delta\theta)^2 \; . \tag{4}$$

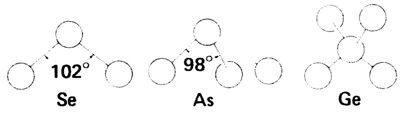

FIG. 3. Elements of local order for a-Se, a-As, and a-Ge. The angles indicated in the structures are obtained from the RDF studies (Refs. 26–28).

The equations for the vibrational frequencies associated with the local clusters of Fig. 3 are given in Ref. 29. In our application of a density-of-states construction we separate the task into two steps. The first concerns the number of features in the density of states and their relative frequencies. Here we are concerned with an explanation for the occurrence of structure in two distinct frequency regimes in *a*-As and *a*-Se and three regimes in *a*-Ge. The second element of concern is in the relative linewidths. In *a*-As and *a*-Se the full widths at half-peak-height, $\Delta\nu$, for the highest-frequency modes are easily determined from the spectra by direct observation and are 58 cm^{-1} for *a*-As and 38 cm^{-1} for *a*-Se. For *a*-Ge we estimate a width of ~ 80 cm^{-1}. We consider two contributions to the linewidth, one associated with the quantitative disorder in the local cluster, i.e., the spread in vibrational frequencies associated with Δr_0 and $\Delta\theta_0$, and a second associated with the interactions with other clusters, i.e., the solid state or medium effects. The second contribution cannot be calculated in our model, but can be quantified within the context of an approximation in which the total experimental linewidth has only the two contributions cited above, i.e., a $\Delta\nu_Q$ associated with quantitative disorder and a $\Delta\nu_M$ associated with other effects of the medium. The second of these contributions is what is obtained in Thorpe's calculation[24]; the first of these has not been considered in any model in a direct way, although it certainly is a contributing element in the network calculations of Alben *et al.*[16]

For each of the clusters of Fig. 3 we have calculated a set of vibrational frequencies using the two-parameter VFF model.[29] In Fig. 4 we present the results of these calculations; we have plotted normalized frequencies $\bar{\nu}_j$, scaled to the frequency of the highest frequency mode, as a function of k_r/k_θ. Our purpose in presenting the results of the calculation in this format is to determine whether the relative frequencies are critically dependent on a particular choice of a force-constant ratio, or whether they are more independent of this ratio. The range of k_r/k_θ considered, $20 \geq k_r/k_\theta \geq 4$, spans the range of force-constant ratios reported for other applications of VFF models. It is clear that the gross features in the frequency spectrum are not critically dependent on the force-constant ratio. In order to compare the experimental spectra of Fig. 2 with this phase of our density-of-states model, we make one simplifying assumption. We assume that well-separated modes retain their identity in the absorption spectrum but that closely spaced modes may be sufficiently broadened so as to lose their identity and contribute to a single feature in the spectrum. For purposes of our comparisons this closeness criterion will be of the order of $\bar{\nu}_i - \bar{\nu}_j \approx 0.1$.

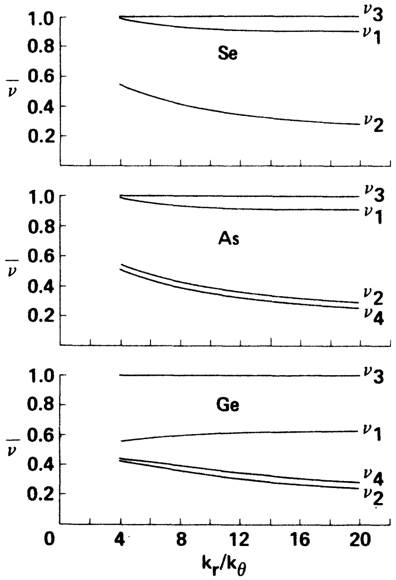

FIG. 4. Normalized vibrational frequency $\bar{\nu}$ as a function of the ratio k_r/k_θ for the molecules that characterize the short-range order in *a*-Se, *a*-As, and *a*-Ge.

If we use this criterion for observability, then the results of this calculation account for the number of frequency regimes in which absorption occurs. Specifically we expect two distinct bands in the absorption spectra of *a*-Se and *a*-As, but three in *a*-Ge; this is just what we have noted in our earlier discussions. In the next paragraphs we consider these comparisons in somewhat greater detail.

Consider first the case of Se, where a bent triatomic "molecule" is used to specify the local cluster. This molecule has three vibrational modes, two of which, ν_1 and ν_3, are predominantly bond-stretching modes, and one of which, ν_2, is a bond-bending mode. ν_1 and ν_3 are near degenerate over the entire range of force-constant ratios considered, whereas their average frequency $(\nu_1+\nu_3)/2$ is approximately two to three times larger than ν_2. There are two dominant features in the first-order ir absorption in *a*-Se, these occur at 254 and 138 cm^{-1}.[4,11] If we set 254 cm^{-1} $= (\nu_1+\nu_3)/2$, we find the force-constant ratio that gives $\nu_2 = 138$ cm^{-1} is $k_r/k_\theta \approx 8$. This ratio is approximately the same as that used in calculations of the lattice dynamics of trigonal Se.[30,31] We propose that the ir absorption of *a*-Se then reflects structure in the vibrational density of states in both the bond-stretching and bond-bending regimes. The Raman spectrum of *a*-Se is dominated by a broad peak near 250 cm^{-1}, then a gap with no scattering from about 200 to 150 cm^{-1}, and finally continuum of scattering below a shoulder at about 140 cm^{-1}, so that the Raman spectrum also gives features in two well-separated frequency regimes. The differences in the details of the two spectra then reflect the different matrix elements for the vibrational modes in the ir and Raman spectra.

Now we consider a-As; the model calculation based on an As_4 pyramidal molecule gives two pairs of modes, ν_1 and ν_3, and ν_2 and ν_4, in two well-separated frequency regimes. ν_1 and ν_3 are bending modes. As we pointed out earlier, the ir absorption of a-As shows dominant features in two well-separated frequency regimes, near 230 cm^{-1} and between 150 and 110 cm^{-1}. From Fig. 4 we find that a force-constant ratio of $k_r/k_\theta \sim 4$ yields the observed frequency ratio. There are as yet no calculations of the lattice dynamics of crystalline As with which to compare this ratio. Raman scattering has been reported for thin films of a-As by Lannin.[32] He also finds structure in the same two spectral regimes, so that the Raman scattering supports our interpretation of the ir absorption.

Finally, we turn to Ge; here the results of our model calculation are significantly different. Instead of modes in two frequency regimes, we find modes in three well-separated regions. As in the case of Se and As, the gross characteristic of the model is essentially independent of the force-constant ratio. Therefore it is more an intrinsic characteristic of the geometry rather than an arithmetical accident associated with a particular choice of force constants. Using the absorption data of either Ref. 9 or Ref. 7 we find that a force-constant ratio $k_r/k_\theta \approx 16$ gives an excellent fit to the center frequencies of the three structures in the ir spectrum. The ratio of 16 is in excellent agreement with the calculations for crystalline Ge by Keating[33] and Martin.[34] The frequencies we find here are also in good agreement with the features that are found in the random-network density-of-states calculation of Alben *et al.*,[16] who used an equivalent two-parameter force-constant model.[33] For the Ge calculation ν_2 and ν_4 are bond-bending modes, ν_3 is a bond-stretching mode in which adjacent atoms move in phase opposition, and ν_1 is a stretching mode in which the central atom of the tetrahedron is at rest. These last two differences in the atomic motions account for the large frequency difference in ν_1 and ν_3. In contrast, for the three- and four-atom local clusters that are used to represent the local order in a-Se and a-As, respectively, there are no modes in which any one atom is at rest. For the physically interesting range of force-constant ratios that we have considered for the Se and As clusters, this precludes large frequency differences between pairs of bond-stretching or bond-bending modes, so that vibrational frequencies are constrained to two separated frequency regimes.

We now turn to the question of linewidth. For illustrative purposes we base our discussion on the characteristic features of the highest-frequency mode in the ir spectrum; these occur at ~ 230 cm^{-1} in a-As, ~ 254 cm^{-1} in a-Se, and ~ 270 cm^{-1} in a-Ge. The fractional half-widths of these modes $\Delta\bar{\nu}$ ($\equiv \Delta\nu/\nu$) are 0.15 for a-Se, 0.23 for a-As, and ~ 0.3 for a-Ge. As one might anticipate these widths scale with increasing coordination, which is a reflection of the local geometry changing from one to two to three dimensional as the local coordination increases from twofold to threefold to fourfold. Using the previous assumption of two independent contributions to the linewidth, we may write

$$\Delta\bar{\nu}^2 = \Delta\bar{\nu}_Q^2 + \Delta\bar{\nu}_M^2 \ . \tag{5}$$

There are two tests for the validity of this equation: One is that $\Delta\bar{\nu} > \Delta\bar{\nu}_Q$, which may be calculated by considering the information contained in the RDF; the second is that $\Delta\bar{\nu}_M$ should scale with the coordination number N ($N=2$ for Se, 3 for As, and 4 for Ge).

The RDF's for a-Se,[26] a-As,[27] and a-Ge,[28] all imply that the variation in θ_0 is more important than the variation in r_0; specifically $\Delta r_0/r_0 \sim 0.01$, whereas $\Delta\theta_0/\theta_0 \sim 0.1$. For each of the local clusters in Fig. 3, we then calculate the frequencies for different θ_0, and as a function of k_r/k_θ. For purposes of comparison and to emphasize the general conclusions that can be drawn from this approach we restrict our comparison to the highest-frequency ir-active modes, $\bar{\nu}_3$ in each of these structures. For a-Se and a-As we use a force-constant ratio of 8, and for a-Ge, 16; for a-Se and a-As, we use a $\Delta\theta_0$ of ± 8° (Refs. 26 and 27), for a-Ge, ± 10° (Ref. 28). The results we present in the next paragraph do not rely critically on this particular choice of parameters. For the analysis that follows, we define $\Delta\bar{\nu}_Q$ by the following equation:

$$\Delta\bar{\nu}_Q \equiv \frac{|\nu_3(\theta_0+\Delta\theta_0) - \nu_3(\theta_0-\Delta\theta_0)|}{\nu_3(\theta_0)} \ . \tag{6}$$

This calculation is made for a given value of k_r/k_θ and takes into account the removal of the degeneracies that occurs when the Ge local cluster is distorted from a perfect tetrahedron. For that case $\nu_3(\theta_0 \pm \Delta\theta_0)$ are frequencies tnat have their "parentage" in the ν_3 mode of the perfect tetrahedral cluster.

From the absorption spectra in Fig. 2 we find that $\Delta\bar{\nu}$, the normalized linewidth, increases in going from Se to As to Ge. $\Delta\bar{\nu}_Q$, the contribution calculated from quantitative disorder, is about twice as large in a-As and a-Ge as in a-Se, but nevertheless satisfies our first criterion that it be smaller than $\Delta\bar{\nu}$. Finally, the values of $\Delta\bar{\nu}_M$, calculated from Eq. (5), show the predicted variation with increasing coordination, $\Delta\bar{\nu}_M$ increasing approximately linearly with N, according to a relationship $\Delta\bar{\nu}_M \sim 0.07N$. This satisfies our second criterion. There is also a simple check for the self-consistency of our results. We can estimate the force constant associated with the linewidth contribution of the medium k_M; we expect this to be less than the bond-stretching force constant, but of the same order as a bond-bending force constant. The medium force constant can be simply related to the bond-stretching force constant by comparing the linewidth to the center frequency, i.e.,

$$\frac{k_M}{k_r} \approx \frac{\Delta\nu_M}{\nu_j} \equiv \Delta\bar{\nu}_M \ . \tag{7}$$

This yields force constants k_M that are clearly less than k_r, but that are approximately the same size, or larger than k_θ. For *a*-Se, $k_M \approx k_\theta$ as one might expect; i.e., for a two-coordinated material we expect the local clusters to be coupled primarily through a bond-bending type of force constant. For *a*-As and *a*-Ge, $k_M > k_\theta$; this reflects the increased coordination of the network, which introduces stronger interatomic forces into the coupling phenomena, e.g., stretching as well and bending contributions.

See Table I for a summary of experimental and calculated results.

TABLE I. Experimentally determined linewidths $\Delta\bar{\nu}$ for *a*-As, *s*-Se, and *a*-Ge. Also included are the linewidth from quantitative disorder, $\Delta\bar{\nu}_Q$, and from the medium, $\Delta\bar{\nu}_M$. $\Delta\bar{\nu}_Q$ is obtained from the VFF calculation, whereas $\Delta\bar{\nu}_M$ is obtained from Eq. (5).

	$\Delta\bar{\nu}$	$\Delta\bar{\nu}_Q$	$\Delta\bar{\nu}_M$
a-Se	0.15	0.062	0.14
a-As	0.23	0.117	0.20
a-Ge	0.30	0.124	0.27

IV. SUMMARY

We have measured the ir transmittance and reflectance of bulk samples of *a*-As. We find a frequency-independent reflectance of 0.29, which in turn gives a dielectric constant of 11.1; this value is in excellent agreement with studies on thin films of *a*-As.[35] We find considerable structure in the ir absorption with the dominant first-order features at 230, 145, and 115 cm^{-1}. Sharp, but very much weaker structure also is present at 283 and 162 cm^{-1}.

Comparisons of the ir absorption of *a*-As and *a*-Se and *a*-Ge yield the following results: The spectrum of *a*-As is similar to *a*-Se in the number of features; however, the integrated absorption or contribution of the ir modes to the dielectric constant is larger. In contrast, the absorption spectrum of *a*-Ge shows features in three frequency regimes rather than two, and those make an even larger contribution to the dielectric constant.

The absorption in *a*-As was discussed within the framework of a density-of-states description. We have developed a model for the density of states that is based on the local order. The usefulness of this model for real amorphous solids is demonstrated by its application to *a*-Se and *a*-Ge as well as *a*-As. In the model the number of gross features to be expected in the ir and Raman spectra is obtained from a consideration of an idealized local order, as shown in Fig. 3 and as determined from RDF studies. The effective width of spectral features is then determined by two effects: the quantitative disorder in the local cluster, principally in the bond angle, and the incorporation of these local clusters into a network structure in which the clusters interact through covalent rather than van der Waals bonds. The contributions from the medium scale with coordination as one would have anticipated. We emphasize that although this approach involves local clusters, the consideration of medium effects allows us to bridge the gap between the "molecular" approach that was previously applied to compound amorphous solids[36-38] and the density-of-states approach that has been applied to *a*-Ge and *a*-Si.[7,15]

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